Nanostructural Engineering of Organic Aerogels

R. W. Pekala
C. T. Alviso
X. Lu
R. Caps
J. Fricke

Lawrence Livermore National Laboratory

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R.W. Pekala and C.T. Alviso, Chemistry & Materials Science Department,
Lawrence Livermore National Laboratory, Livermore, CA 94550

X. Lu, R. Caps, and J. Fricke, Physikalisches Institut der Universitat Wurzburg,
Am Hubland, D-97074 Wurzburg, Germany

ABSTRACT

Aerogels are a special class of open-cell foams with an ultrafine cell/pore size
(<50 nm), high surface area (400-1100 m^2/g), and a solid matrix composed of
interconnected colloidal-like particles or fibers with characteristic diameters of 10
nm. This paper examines the correlation between nanostructure and thermal
conductivity in a series of resorcinol-formaldehyde (RF) aerogels prepared under
different synthetic conditions.

INTRODUCTION

Aerogels have a unique morphology in that *both* the covalently-bonded particles of the solid phase and the interconnected pores of the gas phase have nanometer-sized dimensions. This nanostructure can be engineered through control of the initial sol-gel polymerization conditions. The polycondensation of (1) melamine with formaldehyde, (2) resorcinol with formaldehyde, and (3) phenolic with furfural are three proven synthetic routes for the formation of *organic aerogels*. The latter two materials can also be pyrolyzed in an inert atmosphere to give carbon aerogels [1-7].

The structure and properties of organic aerogels are analogous to their inorganic counterparts (e.g., silica). These materials have continuous porosity, an ultrafine cell/pore size ($\leq$ 50 nm), high surface area (400-1100 m^2/g), and a solid matrix composed of interconnected colloidal-like particles or fibrous chains with characteristic diameters of 10 nm. This nanostructure is responsible for the unique thermal, acoustic, optical, electrical, and mechanical properties of aerogels.

A major advantage of organic aerogels is their low Z (atomic number) composition. In general, most polymers have lower thermal conductivities than inorganic glasses, and this same trend would be expected for aerogels having such compositions. Recently, we showed that resorcinol-formaldehyde aerogels are even better thermal insulators than silica aerogels when measured under ambient conditions [8]. A record low thermal conductivity value of 0.012 W/m-K was obtained at a density of 160 kg/m^3. In contrast, silica aerogels have a minimum thermal conductivity of 0.016 W/m-K under ambient conditions. These data demonstrate the importance of controlling both the composition and structure of aerogels.

In this paper, we have extended the previous study to examine the correlation between nanostructure and thermal conductivity in a series of resorcinol-formaldehyde (RF) aerogels prepared under different synthetic conditions. Thermal conductivity measurements were performed on monolithic samples (2.5 x 2.5 x 10 cm^3) using a hot-wire device. The measurements under variation of gas pressure as well as infrared transmission data allowed the determination of

the solid, gaseous, and radiative thermal conductivity as a function of bulk density and the underlying nanostructure. Our results show that the thermal conductivity components are clearly correlated with the structure of aerogels as follows: (1) bulk density and particle interconnectivity determine the solid conductivity, (2) the pore size influences the gaseous conductivity, and (3) the radiative transport depends on the mass specific infrared absorption of the polymer repeat units.

EXPERIMENTAL

The preparation of RF gels involved mixing the starting reactants in a 1:2 molar ratio as described previously [6]. Deionized and distilled water was then added as the diluent to form gels having concentrations of 5-50 % w/v. Sodium carbonate was used as a weak base catalyst. After stirring to form a homogeneous solution, the mixture was poured into glass molds, sealed, and cured for 3-7 days at 85 °C. Upon completion of the cure cycle, the crosslinked gels were removed from their glass molds, and the pore fluid (i.e., water) was exchanged with acetone. The acetone-filled gels were then placed in a jacketed pressure vessel, exchanged with liquid carbon dioxide, and supercritically dried (T_c= 31 °C; P_c= 7.4 MPa).

The thermal conductivity measurements were performed using a hot-wire apparatus [9]. A platinum wire was squeezed between a pair of identical aerogel blocks, and it served as both heating element and temperature sensor. The temperature increase during a heat pulse was recorded, and the data were used to extract the thermal conductivity under ambient conditions. Data were also recorded as a function of gas pressure. The infrared spectral extinction of the samples was used to determine their radiative conductivity.

RESULTS AND DISCUSSION

The [Resorcinol]/[Catalyst] (R/C) ratio of the starting solution is the dominant factor which affects the nanostructure of RF aerogels. Transmission electron microscopy shows that these aerogels are composed of interconnected colloidal-like particles derived from RF clusters formed in solution. Under high catalyst conditions (i.e., R/C=50), the particles have diameters of 3-5 nm and are joined

together with large necks, giving the aerogel a fibrous appearance. Under low catalyst conditions (i.e., R/C=200, R/C=300), the particles have diameters of 11-14 nm and 16-20 nm, respectively. These aerogels have a "string of pearls" appearance in which there is only a small neck region between the interconnected particles [4].

Differences in nanostructure are reflected in the mechanical properties of the above RF aerogels [10]. As expected, both the compressive modulus and strength increase with decreasing particle size and improved particle interconnectivity. As such, RF aerogels exhibit a distinct rank order when modulus or strength is compared at any given density: R/C=50 > R/C=200 > R/C=300. At equivalent densities, RF aerogels prepared at R/C=50 are approximately 7X stiffer that RF aerogels prepared at R/C=300, indicative of a more 'structurally efficient' nanostructure for the former samples.

The thermal transport through porous materials can be described as

$$\lambda_{total} = \lambda_s + \lambda_g + \lambda_r \,, \qquad\qquad [1]$$

where λ_s is the solid conductivity, λ_g is the gaseous conductivity, and λ_r is the radiative contribution. RF aerogels that are >1 cm thick provide enough IR absorption to be considered optically thick, and the specific extinction e (~50 m^2/kg) is independent of the polymerization conditions (i.e., R/C ratio). The radiative contribution to the heat transfer for RF aerogels with $\rho \approx 100$ kg/m^3 is $\lambda_r \approx 0.002$ W/m-K at room temperature. For higher densities, the radiative contribution is even less because $\lambda_r \propto \rho^{-1}$.

The RF nanostructure, as reflected in the interconnectivity of the particles and pores, is expected to influence both the solid and gaseous conductivities. Figure 1 shows the solid thermal conductivity of various RF aerogels versus bulk density in a double log plot. The following power-law relationship is observed

$$\lambda_s \propto \rho^{\,\delta} \,, \qquad\qquad [2]$$

where $\delta \approx 1.2$ for RF aerogels prepared at R/C=50 and $\delta \approx 1.5$ for RF aerogels with R/C =200 and R/C=300. The interconnections between particles of the solid

matrix are particularly important for the solid conductivity, and λ_s increases as the R/C ratio decreases and the particle interconnectivity improves.

Figure 2 shows the gaseous conductivity at ambient conditions, derived by subtracting the radiative and solid conductivity contributions from λ_{total}, for RF aerogels as a function of bulk density. At all R/C ratios, the gaseous conductivity decreases with increasing density , and the average pore diameter ϕ varies according to $\phi \propto \rho^{-0.8}$. At a fixed aerogel density, the gaseous thermal conductivity λ_g is lower for samples prepared at R/C=50 compared to those at R/C=200 and R/C=300. These data indicate that the pore size is smaller for the R/C=50 samples, but in all cases ϕ is less than the mean free path of air ($\approx$70 nm). This nanoporosity provides the key to the low thermal conductivity of aerogels --- gas molecules have a higher probability of elastic collisions with the solid matrix than they do in colliding with each other. This suppression of gaseous conduction means that λ_g for RF aerogels is less than the value for non-convecting air (i.e., 0.026 W/m-K).

The competing effects of the particle interconnectivity and pore size upon the total thermal conductivity can be observed in Figure 3. At each R/C ratio, a flat minimum in λ_{total} is observed as a function of density. This minimum occurs because the solid conductivity increases monotonically with density, while the gaseous and radiative conductivities decrease with density. The density for minimal total thermal conductivity increases slightly with increasing R/C ratio. The lowest thermal conductivity 0.012 W/m-K was obtained for an RF aerogel synthesized at R/C=200.

SUMMARY

Aerogels are two-phase materials in which both the interconnected particles and pores have nanometer-sized dimensions. This intricate structure is responsible for the partial suppression of gaseous conduction and elimination of convection, resulting in extremely low thermal conductvity values. Our data indicate that the thermal conductivity components are correlated with the bulk density and R/C ratio, thereby permitting us to manipulate polymerization conditions to optimize thermal performance.

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